

Certification of Trimethyllead in Aqueous Calibrant Reference Materials (GBW(E)080971 and GBW(E)080972)

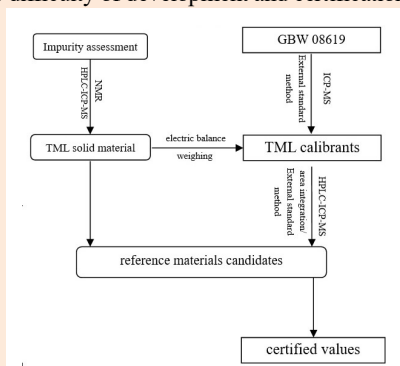
Hai LU, Jun WANG,* Chao WEI, Jingbo CHAO, Tao ZHOU, and Motian ZHAO

Division of Chemical Metrology and Analytical Sciences, National Institute of Metrology, Beijing 100029, P. R. China

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ABSTRACT: Certified Reference Materials (CRMs) are a widely recognized tool for the comparability of measurements taken in different times and spaces through their “traceability chain”. However, aqueous CRMs used as calibrants which allow tracing to the SI units are urgently needed especially for the speciation analysis CRMs due to the difficulty of development and certification for them. Herein, we presented two new aqueous trimethyllead reference materials. In the certification campaign, two important steps were included: 1) a traceability chain to the standard reference material GBW08619 which is a primary Pb(II) calibrant solution was set up; 2) isotopic variations of lead in trimethyllead (TML) and GBW08619, were introduced to the certified values and combined uncertainties. This paper describes in detail the homogeneity and stability studies, impurity assessment with nuclear magnetic resonance spectroscopy (NMR) and high-performance liquid chromatography - inductively coupled plasma mass spectrometry (HPLC-ICP-MS), traceability assurance protocol and the inter-laboratory co-certification campaign for the certification of their TML contents. Consequently, two CRMs (GBW(E)080971: $(92.73 \pm 3.15) \mu\text{g g}^{-1}$ as Pb, $k=2$ and GBW(E)080972: $(0.740 \pm 0.030) \mu\text{g g}^{-1}$ as Pb, $k=2$) are now available.



INTRODUCTION

One of the key properties of accurate results is comparability - the ability to compare with each other no matter where they originate. Generally, comparability is provided by tracing to a consistent and agreed measurement unit or scale. For chemical measurement, this is best illustrated with the mole, the internationally accepted SI unit. Here, traceability is defined as¹: property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty. “Traceability” is therefore a strategy to link individual results to a publicly accepted stable reference, and thus the results can be compared through their relationship and link to the reference.

The use of certified reference materials (CRMs) is a widely recognized tool for the comparability of measurements, undertaken in different times and spaces, through their “traceability chain”. Matrix CRMs can be used to verify the accuracy of analytical techniques, while simple calibration CRMs, especially solution-based CRMs, are more important in linking the

results to the SI directly.

Quality assurance for environmental analysis is a growing feature of the 21st century. During the past decades, alkyllead materials *e.g.* tetramethyllead or tetraethyllead were used as “antiknocks” in gasoline. Through vehicular and subsequent plant emissions, the alkyllead entered our environment by atmospheric aerosols,² rainwater or water flow.^{3,4} Due to the toxicity effects of organolead species on the liver and nervous system, the USA abandoned the use of leaded gasoline in 1986, while Europe and China abandoned it in 2000. From then on, the rise of the use of non-leaded gasoline has led to a declining consumption of organolead compounds world-wide. However, it is recently back in focus following renewed interests in studies on aquatic products,⁵ algae,^{6,7} blood and urine,⁸ tobacco and tobacco products,⁹ soil,¹⁰ bovine serum,¹¹ sea water,¹² groundwater,¹³ and polluted water,¹⁴ sediments,¹⁵ body tissues of rats,¹⁶ Antarctic krill, and fish.¹⁷ Tetramethyllead can readily degrade into trimethyllead and then dimethyllead and finally, especially when exposed to sunlight, into inorganic lead. Similar degradations occur with tetraethyllead. All of these species are toxic which can affect on a

human's nervous system, especially the brain, and damage organs such as the liver and kidney.

Owing to the health concerns and environment protection, the monitoring of alkyllead species needs to be sustained over a long period. The techniques used are generally based on a combination of different analytical steps, including extraction, derivatization (e.g., ethylation,^{18,19} butylation,^{2,4} propylation,²⁰ pentylation²¹ etc.), separation (e.g. gas chromatography, GC,^{2,4,18-22} high-performance liquid chromatography (HPLC)²³⁻²⁶ or capillary electrophoresis (CE)²⁷) and detection (e.g., atomic absorption spectrometry (AAS),^{4, 20-22, 28} microwave induced plasma-atomic emission spectrometry (MIP-AES)²⁹, inductively coupled plasma-mass spectrometry (ICP-MS),^{2,4,24,25,30} gas chromatography-electron capture detector (GC-ECD)³¹ etc.).

Most techniques mentioned above use external calibration method. Such method depends on "accurate and precise external curve" which must be produced using CRMs or reference materials³² or calibrants that can be directly traced to accepted standards. Additionally, with real samples care is taken to ensure no physical and spectral interferences are present such that response in the matrix sample is identical to that in the external calibration. As previously mentioned, pure calibration CRMs are especially needed. To the best of our knowledge, only an urban dust reference material³³ and an artificial rainwaterreference material³⁴ are available and they were developed many years ago and little information on their validity is available for TML. Two new solution-based trimethyllead (TML) reference materials have now been developed to aid assuring traceability in TML speciation analysis. In order to provide credible traceability, a traceability chain linked to a high purity Chinese lead CRM (GBW08619, (1000±2) µg/g as Pb²⁺, *k*=2) was used. These CRMs serve as standard calibrants having traceability to the SI units. This paper also describes the traceability assurance, homogeneity study, stability study and certification campaign in detail. Further, an uncertainty budget was discussed involving all sources. Two CRMs (GBW(E)080971: (92.73 ± 3.15) µg g⁻¹ as Pb²⁺, *k*=2 and GBW(E)080972: (0.740 ± 0.030) µg g⁻¹ as Pb²⁺, *k*=2) are now available.

EXPERIMENTAL

Reagents. (CH₃)₃PbBr was purchased from Alfa Aldrich, USA for preparation of the CRM candidates. A reference material (GBW08619, National Institute of Metrology, China) which is a stabilized aqueous solution of lead was adopted to calibrate the standard TML curve by HPLC-ICP-MS. An isotopic ratio CRM, NIST 981 developed by National Institute of Standards and Technology, USA was performed to calibrate the isotopic composition of Pb in TML.

Preparation of the CRMs. Two aqueous TML CRMs were gravimetrically prepared with (CH₃)₃PbBr and de-ionised water. (CH₃)₃PbBr was weighed by an electronic balance (M 6, capacity up to 2.1 g and readability 0.1 µg, made by METTLER TOLEDO, Swiss) and flask bottles (250 mL, made by Sinopharm Group, China). De-ionised water (18 MΩ cm) was obtained from a Millipore water purification system (Elix 5 UV, Milli-Q Element A10, Millipore Corporation, Billerica, MA, USA).

Brown glass ampoules, glass pipette, mini quartz beaker and other tools were all cleaned thoroughly with distilled HNO₃ and de-ionised water. HNO₃ was obtained from BVIII grade HNO₃ by distilling under sub-boiling conditions. BVIII grade HNO₃ was purchased from Beijing Institute of Chemical Reagents, China.

Firstly, a solution was prepared by weighing 42.999mg (CH₃)₃PbBr and diluting into 250 mL flask bottle with de-ionised water. Subsequently, a solution A with the concentration of approximate 107 mg L⁻¹ as Pb²⁺ was achieved. Then, 2 mL of solution A was transferred by a pipette into another 250 mL flask bottle and diluted with de-ionised water, too. Consequently, 2 TML reference material candidates named H (high level) and M (middle level) which will be mentioned later were prepared.

Reference material candidates were sub-bottled in brown glass ampoules, each containing 2 ml of solution. The bottles were flame sealed by a home-made automatic sealing machine. Subsequently, 120 bottles were achieved. Ampoules were selected randomly for homogeneity tests, stability tests and certification during the development process.

Instrumental conditions. An ICP-MS (Agilent 7500c, Agilent Technologies, Co. USA) combined with a HPLC (Agilent 1100, Agilent Technologies, Co. USA) equipped with a C18 column, Zorbax Eclipse XC18, 25cm×4.6mm was performed for certification, homogeneity test and stability tests. The mobile phase was 30% MeOH (analytical grade, Beijing Chemical Reagents Co., China) and 70% buffer (acetic acid + NH₄Ac, pH=4.6, analytical grade, Beijing Chemical Reagents Co., China).

²⁰⁸Pb was monitored for quantitatively determining the concentration of TML in reference material candidates. As no isobaric interferences on ²⁰⁸Pb during ICP-MS measurement of the aqueous solution, no collision gas was introduced. 10% O₂ was introduced into the ICP torch to reduce the CH₃OH. The nebuliser employed was a Meinhard nebuliser made by GE Inc, USA. The spray chamber was cooled down to -5°C with a recirculating chiller. The ion lens settings were optimized every day to give the best performance.

Traceability Protocol. CRMs can guide the traceability of results conveniently because their purity and concentrations have been achieved by following precise rules and guidelines for

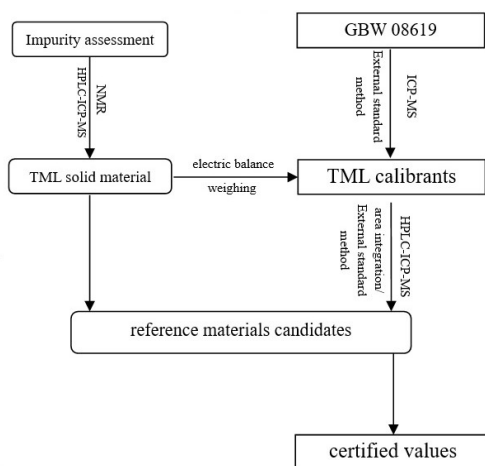


Fig. 1 Framework of Traceability Protocol for Certification of TML in CRMs.

exogenous lead species especially inorganic Pb should be confirmed.

In the traceability protocol mentioned above the assumed concentrations of the target TML CRMs were re-calibrated against the inorganic GBW08619 lead CRM. This implied that any other species of lead except for the TML must not be present. We assessed the TML reagent with nuclear magnetic resonance spectroscopy (NMR, 300M, Varian Corp. USA) and HPLC-ICP-MS (HPLC: Agilent 1100, Agilent Technologies, Co. USA, equipped with a C18 column, Zorbax Eclipse XC18, 25 cm×4.6mm, mobile phase: 30% MeOH, analytical grade, Beijing Chemical Reagents Co., China and 70% buffer (acetic acid + NH₄Ac, analytical grade, Beijing Chemical Reagents Co., China), pH=4.6; ICP-MS: Agilent 7500c, Agilent Technologies, Co. USA). NMR was used to evaluate if any other organolead compounds were present while HPLC-ICP-MS was used for determining if inorganic Pb²⁺ ions were present.

Both H (hydrogen)-NMR and C (carbon)-NMR spectrometry were used and no other peaks were detected except for TML (Fig. S1 and S2). Furthermore, there was no peak for Pb²⁺ when checked by HPLC-ICP-MS. This implied that the re-calibration protocol was reasonable owing to no other organolead, *i.e.*, tetramethyllead, triethyllead, dimethyllead, methyllead, and Pb²⁺ were present.

It was concluded, therefore, that the TML reagent wasn't degraded or contaminated by Pb²⁺. Subsequently, the purity of TML reagent could be reliably determined directly by ICP-MS using GBW08619 as an external standard method. A purity of (CH₃)₃Pb⁺ (85.3 ± 1.9 %, *k*=2) was achieved which was the average of 4 independent determinations of 5 ng mL⁻¹, 15 ng mL⁻¹, 25 ng mL⁻¹ and 50 ng mL⁻¹ solutions prepared by the TML reagent. The uncertainty derived from the replicate measurement of purity will be carried into the combined uncertainty of the CRMs.

As to the 14.7% impurities, it was assumed that maybe they were organic compounds or inorganic salts. However, they will not affect the fraction of TML in the CRMs based on the assessment of HPLC-ICP-MS and NMR.

Analysis of the Isotopic Composition of Lead in TML. Owing to isotopic fractionation in nature, the isotopic composition of lead in the TML had to be determined before certification. Consequently, the uncertainty of the isotopic variation of Pb should be considered in the combined uncertainty of the CRMs. A multi-collector ICP-MS (MC-ICP-MS, Isoprobe, GV Instruments, UK) was used to determine the isotopic composition of the TML candidate CRM solutions. Mass bias of the MC-ICP-MS was corrected for using NIST 981 CRM based on a sample-standard bracketing (SSB) method. The results show that isotopic composition of lead differ amongst the CRMs and the TML stock material. Fig. 2 shows the variations in isotopic abundance. The

Fig. 2 Variation of Lead Isotopes in NIST 981, GBW 08619 and TML.

development of CRMs, such as ISO Guide 17034. In the development campaign for two TML RM candidates, the certification process employed an area integration method using HPLC-ICP-MS. A stock solution of TML was prepared with (CH₃)₃PbBr after impurity assessment and used as standard calibrants. The concentration of stock solution was re-calibrated using an inorganic lead reference material (GBW08619, National Institute of Metrology, China) by a quadrupole ICP-MS (Agilent 7500c, Agilent Technologies, Co. USA). Fig. 1 shows the traceability chain from the inorganic lead CRM to the values of the developed aqueous TML CRMs.

Impurity assessment with HPLC-ICP-MS, NMR and ICP-MS. Typically, a mass balance method³⁵ is performed for determining the mass fraction of organic and inorganic components in a high purity material with several techniques. In this certification of TML reference materials, it's not necessary to achieve all impurities including organic compounds and inorganic species while the total purity should be determined and no

Table 1. Budget of Relative Uncertainties for two CRM candidates

uncertainties	H candidate	M candidate	type
$u_{SB} (k=1)$	0.007	0.008	A
$u_{homo} (k=1)$	0.0077	0.0095	A
$u_{stab} (k=1)$	0.006	0.011	A
$u_{cc} (k=1)$	0.0025	0.0025	A
$u_{purity} (k=1)$	0.012	0.012	A
$u_{CRM} (k=1)$	0.004	0.004	B
$u_{weighing} (k=1)$	0.0012	0.0014	B
$u_{iv} (k=1)$	0.00070	0.00070	A
Combined uncertainty (k=1)	0.017	0.020	
Extended Uncertainty (k=2)	0.034	0.040	

Table 2. Normalized results of the stability study

Time ^a	Rt ± Ut	
	M	H
1	1.020±0.047	1.013±0.028
3	1.011±0.034	1.021±0.031
6	1.014±0.044	1.027±0.030
9	1.003±0.034	0.999±0.032
12	1.016±0.040	1.012±0.031

^a month

atomic weight of Pb in TML, Ar = 207.21, is subsequently achieved, which agrees well with those of the NIST 981 (Ar = 207.22) and GBW 08619 (Ar = 207.21). Ultimately, the concentrations of candidate H and M calibration CRMs were recalculated based on the atomic weight of lead, and the uncertainty of isotopic variations was carried into the combined uncertainties.

RESULTS AND DISCUSSION

Homogeneity Study. Eleven bottles both for between-bottle homogeneity study and within-bottle homogeneity study were all selected randomly according to the Technical Norm of Primary Reference Material (JJF 1006–1994),³⁶ which is equivalent to ISO 17034.

The between-bottle homogeneity of the candidate samples was checked by determining TML in each of 10 bottles by HPLC-ICP-MS. The within-bottle homogeneity was verified by 3 replicate analyses from one bottle by HPLC-ICP-MS as well. The samples were first diluted to approximately 10 ng g⁻¹ before being analysed.

The Statistical Variance Analysis at a significance level of 0.05 did not show any significant differences between the within-bottle and the between-bottle data ($F_{test,0.05(9,10)} = H_{candidate}: 0.66 / M_{candidate}: 2.48$). Following these results, the materials were considered to be homogeneous. The uncertainties associated with the between and within variation were summarized in Table 1. The uncertainties will be convoluted into the combined uncertainties.

Stability Study. All candidate CRMs were sealed in brown ampoules and stored in a dark and temperature controlled (<4°C)

environment in order to keep their stability.

TML in candidate CRMs was determined at the beginning of the storage period and after 1, 3, 6, 9, and 12 months. The same analytical procedures that were used for the homogeneity study were performed.

Instability would be detected by comparing the concentrations of TML determined at the beginning of the storage period ($t=0$) with the concentrations determined during the stability study program. The results obtained at $t=0$ were used as a reference for the results obtained at each time period of analysis ($t=1, 3, 6, 9,$ and 12 months). Table 2 shows the ratios (R_t) of the mean values ($X_{t=0}$) for five replicate measurements determined at the beginning of the storage period ($t=0$) to the mean values ($X_{t=i}$) from four or five replicate determinations made during the stability study procedure, here, $R_t = X_{t=0} / X_{t=i}$.

The uncertainty of stability study u_{stab} (formula (1)) was calculated from the relative standard deviation (RSD, %) of replicate measurements obtained during each stability study period:

$$u_{stab} = \sqrt{RSD_{t=0}^2 + RSD_{t=i}^2} \times R_{t=i} / 100 \quad (1)$$

The ideal stability would be awarded the ratio $R_t=1$. However, there were some random variations during the speciation analysis procedure. The value must fall between $R_{t=i} - u_{t=i}$ and $R_{t=i} + u_{t=i}$. If R_t showed an increasing deviation, it implied an instability within the sample. On the basis of all the results, it was concluded that no instability was found for H candidate and M candidate.

Otherwise, a t -test method was performed to propose the stability. As for the R_t test mentioned above, the results obtained on the samples at $t=0$ were also used as reference for the results obtained at each occasion of stability study ($t=1, 3, 6, 9$ and 12 months). Each result measured at each occasion of stability study were calculated with the formula (2):

$$t = \frac{|\bar{X}_1 - \bar{X}_2|}{\sqrt{\frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2} \times \frac{n_1 + n_2}{n_1 n_2}}} \quad (2)$$

Where \bar{X}_1, S_1, n_1 represent the mean value, standard deviation and replicates of samples at $t=0$, respectively. \bar{X}_2, S_2, n_2 represent the mean value, standard deviation and replicates of samples at $t=t_i$ respectively.

The t -test furtherly showed that there was no instability for the H and M candidate within 12 months. Therefore, both H and M candidate were used in the next inter-laboratory co-certification campaign.

Table 3. Certified values of TML in two CRM candidates ($\mu\text{g g}^{-1}$ as Pb)

Candidate	Certified value	Uncertainty
M	0.740	0.030
H	92.73	3.15

Inter-laboratory Co-certification. An inter-laboratory study was organized for the certification exercise. Five bottles of each candidate CRM were shipped to the participating laboratories. Each laboratory was requested to perform at least 3 independent replicate determinations on each bottle. The pilot laboratory provided all the participants with the TML reagent which had previously been analysed by NMR spectrometry and HPLC-ICP-MS to ascertain its purity.

Due to the inherent difficulty in the extraction and derivation procedure required for GC analysis which also could lead to an uncontrolled uncertainty, all participants chose HPLC combined with Q-ICP-MS which is a more sensitive analytical procedure than AAS or other instrumental approaches. IDMS is a primary method that provides results directly traceable to the SI unit system, specifically the mole. But for a speciation analysis procedure, an isotopic species, *i.e.* $(\text{CH}_3)_3^{207}\text{Pb}^+$ must first be synthesized and purified. Then, on the basis of the precise analysis of its structure, it is necessary to determine its concentration accurately. Such procedure is very expensive and complicated and requires experience in the synthesis, purification and use of special instrumentation. During the campaign all the participants chose the external standard method relying on peak area integration to perform the analysis.

Three sets of data were evaluated by statistical tests: the values of within-laboratories, the population of laboratory means on each bottle and the population of all individual results.

All results reported here have undergone technical scrutiny. The sets of results were checked by applying the following statistical tests: normality testing to assess the conformity of the distributions of individual results and of laboratory means to normal distributions; the Dixon test to assess the outlying values of between- and within-laboratory; the Cochran test to detect outliers in the laboratory variances; and the one-way analysis of variance (*F*-test) to compare and estimate the between- and the within-laboratory components of the overall variance of all the individual results. All normality tests implied that all the sets of results showed good agreement. However, the Dixon test had already removed some of the data points used in the within-laboratory and between-laboratory normality tests. When calculating the certified values Cochran's rule was used to assess the conformity of the distribution of individual results and of laboratory means to normal distributions. The estimates of the within-laboratory standard deviation (SW) and the between-laboratory standard deviation (SB) after the Dixon test, as derived from one-way analysis of the variance, demonstrated that the between-laboratory

variation was not significant and much lower than the variation of the within-laboratory (SW). It was therefore decided to base the certification on individual results from each bottle rather than the laboratory means. The certified values were calculated as the arithmetic mean of all remaining individual results after outlier rejection. Combined standard uncertainties of the certified results were obtained by calculating all the individual uncertainty components. The combined uncertainties were calculated with 1) the between-laboratory standard deviation (SB), u_{SB} ; 2) the uncertainty of homogeneity study (u_{homo}); 3) the uncertainty of stability study (u_{stab}); and the uncertainties derived by non-linearity of calibration curves (u_{cc}), uncertainty of the purity determination (u_{purity}), uncertainty of the concentration of the inorganic Pb CRM (u_{CRM}), uncertainty of the weighing ($u_{weighing}$), and the uncertainty of the isotopic variation of Pb (u_{iv}).

The budgets of uncertainties are listed in details in Table 1. Note: 1) all uncertainties including combined uncertainty are calculated as relative standard deviation (RSD); 2) u_{iv} was calculated as RSD of abundance of mass 208 in NBS981, TML and GBW08619; 3) u_{cc} was calculated with the formulas (3 & 4) listed below:

$$u_{cc} = \frac{s}{a} \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_0 - \bar{c})^2}{\sum_{i=1}^n (c_i - \bar{c})^2}} \quad (3)$$

$$s = \sqrt{\frac{\sum_{i=1}^n [I_i - (b + ac_i)]^2}{n - 2}} \quad (4)$$

Here, s : standard deviation of each calibrants; a : slope of calibration curve; b : intercept of calibration curve; p : replicate number of the experiment; n : replicate number of each calibrants; c_0 : concentration of TML in H or M candidate ($\mu\text{g g}^{-1}$ as Pb^{2+}); c_i : concentration of TML in calibrants ($\mu\text{g g}^{-1}$ as Pb^{2+}); \bar{c} : mean of the concentration of TML in calibrants ($\mu\text{g g}^{-1}$ as Pb^{2+}); I_i : signal of each calibrants (cps).

Certified Value. The certified values and their uncertainties (half-width of the 95% confidence interval) are given in Table 3. TML is certified as the mass fraction of $(\text{CH}_3)_3\text{Pb}^+$ ($\mu\text{g g}^{-1}$ as Pb). Candidate H is now authorized as GBW(E)080971 and candidate M as GBW(E)080972.

CONCLUSION

Two aqueous trimethyllead (TML) calibrant reference materials were prepared and certified. In order to control their quality a traceability chain from which the results can be traced to an inorganic lead reference material (GBW 08619) was set up. The certified values were assigned following an interlaboratory intercalibration scheme involving 5 independent laboratories.

After evaluation with statistical analysis including normality testing, Dixon test, and Cochran test the certified values were calculated. Consequently, two CRMs ($(92.73 \pm 3.15) \mu\text{g g}^{-1}$ as Pb, $k=2$ and $(0.740 \pm 0.030) \mu\text{g g}^{-1}$ as Pb, $k=2$) are now available.

ASSOCIATED CONTENT

Supporting information (Figs. S1–S2) is available at www.at-spectrosc.com/as/home

AUTHOR INFORMATION



Dr. Wang Jun, a principal researcher of National Institute of Metrology P. R. China (NIM), Titular member of Commission on Isotopic Abundances and Atomic Weights under IUPAC and Chair of Subcommittee on Isotopic Abundance Measurements. She has been working as the member of editorial board in *Geostandards and Geoanalytical Research* and *Journal of Chinese Mass Spectrometry Society*. She has long been engaged in the research and application of

metrology in chemistry, including study of highly sophisticated measurement techniques for isotope analysis, development of national standards, metrological technical specifications and certified reference materials, and establishment of the metrological traceability system for isotope and chemical component measurements. By achieving the equivalence in CIPM CCQM international comparisons of analytical techniques, nearly 100 items of internationally recognized calibration and measurement capabilities (CMC) have been published in the BIPM KCDB.

Corresponding Author

*J. Wang

Email address: mslab@126.com

Notes

The authors declare no competing financial interest.

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